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POLY(ETHER-IMIDE-BENZOXAZOLE) VIA NUCLEOPHILIC AROMATIC SUBSTITUTION
WITH FLUOROPHENYL/PHENOLIC PRECURSOR Raj A. Sundar, Lon J. Mathias
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2-(4'-Fluorophenyl)-5,6-[N-(hydroxyphenyl)]imidebenzoxazole was prepared from 4-amino-5
hydroxy-N-(4'-hydroxyphenyl)phthalimide. 4,5-dichlorophthalic anhydride was reacted with *p*-
benzyloxylaniline in DMAc followed by thermal cyclization using a toluene azeotrope to give the
dichlorophthalimide in good yields. Reacting the dichlorophthalimide with potassium nitrite in
refluxing DMF gave the nitro-hydroxy-phthalimide. Simultaneous reduction of the nitro group and
deprotection of the benzyloxy group provided the precursor to an imide-benzoxazole. Oxazole
formation with *p*-fluorobenzoyl chloride in NMP afforded an AB monomer. Initial polymerization
efforts using sodium hydride in NMP and CHP were limited by polymer precipitation, although high
polymerization temperatures using CHP gave a higher molecular weight polymer.

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Poly(ether-imide-benzoxazole) via Nucleophilic Aromatic Substitution with Fluorophenyl/phenolic Precursor

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Introduction

Polyimides and polybenzoxazoles have good mechanical and insulative properties as well as high thermal stabilities.¹⁻⁴ These are important for many of today's applications of high performance polymers. Inherent drawbacks of these systems are their insolubility and intractability, leading to difficulties in both synthesis and processing. For these reasons, polybenzoxazoles have only recently been commercialized, while polyimides have been in use for years due primarily to processability of the soluble poly(amic acid) precursors or by the incorporation of flexible spacer groups into the polymer backbone.

Poly(ether-imides) incorporate oxygen spacers in the polymer backbone which make them more soluble and processable than their rigid rod or semirigid counterparts, but with retention of good thermal properties.^{5,6} Poly(ether-imides) based on phthalimides are readily produced by nucleophilic aromatic substitution (NAS) involving phenoxide displacements of halo or nitro groups on activated 4- or 4,5-substituted phthalimides. NAS follows a bimolecular addition-elimination mechanism proceeding through a stabilized intermediate (Meisenheimer complex). The order of displacement is $F = NO_2 > Cl > Br > I$, and the use of alkali earth metal counterion (K, Na) depends on phenoxide solubility. Polar aprotic solvents solubilize both the monomers and polymers, and facilitate NAS polymerization.

Caswell⁷ reported that 4,5-dichlorophthalimides undergoes substitution by KNO_2 to generate 4-nitro-5-hydroxy phthalimides, precursor to the imide-benzoxazole monomers needed for this project. The generation of both nitro and hydroxy substituents on the same substrate is attributed to the ambident nature of the nitrite ion. This provides a one-pot method of multiple functionalization.

Preston and coworkers⁸ reported the synthesis and characterization of a series of poly(imide-benzoxazole)s, which demonstrate good mechanical properties and thermal stabilities (thermal decomposition in 520-625°C range). These imide-benzoxazoles were produced by reacting diamines containing preformed benzoxazole moieties with dianhydrides to produce the soluble poly(amic acid) precursors, which were isolated, fabricated and then thermally cyclized to obtain the desired polymers.

Hedrick and coworkers^{9,10} reported imide-aryl ether-benzoxazole copolymers which were tough and ductile as indicated by both high elongations (70-110 %) and moduli (2300-2650 MPa). Their systems also contained diamines with preformed benzoxazole moieties, but a key feature was their coreactions with 4,4'-oxydianiline (ODA) and pyromellitic dianhydride (PMDA), and the thermal solution cyclization of the poly(amic-acid)benzoxazole in 1-methyl-2-pyrrolidinone (NMP) to generate the soluble poly(imide-aryl ether benzoxazoles). This allowed tailoring of polymers with benzoxazole contents ranging from 10-74 wt-%. Low thermal expansion coefficients (20 vs 35 for PMDA/ODA polyimides) were realized with benzoxazole contents greater than 50 wt-%.

Hedrick and coworkers^{10,11} also demonstrated that 2-(4'-fluorophenyl)benzoxazoles could undergo quantitative nucleophilic aromatic substitution (temperature range of 160-220°C) with various phenoxides and solvent systems. The polymerization was based on the activation by the benzoxazole ring on the 4'-fluorophenyl group towards nucleophilic attack.

Our immediate goals are synthesis and characterization of poly(imide-benzoxazoles) with the imide and oxazole moieties on the same nucleus, and evaluation of processability and properties.

Experimental

4,5-Dichlorophthalic acid was dehydrated with excess acetic anhydride under reflux conditions to yield 1; mp 190°C. 4-Benzylether aniline hydrochloride was condensed with 1 in N,N-dimethylacetamide (DMAc) at 0°C (1h) and at 25°C (8h) using 1-methylpyrrolidine as acid scavenger; dehydraton at 150°C (6h) using a toluene azeotrope afforded 2b; mp 232-235°C. Potassium nitrite was reacted with 2b in N,N-dimethylformamide (DMF) under reflux conditions (24h), the reaction mixture cooled, and 1 equivalent of HCl added to give 3b; 255-257°C. Ammonium formate was reacted with 3b in the presence of Pd/C (10%) in DMAc at 25°C (12h) to obtain 4b; mp 330-335°C. Aniline was reacted with 1 to obtain model compound 2a. Model compounds 3a and 4a were then obtained; mp 2a: 216°C, 3a: 225 - 227°C and 4a: 325 - 327°C. 4-Fluorobenzoyl chloride was added dropwise to a solution of 4b, in NMP, under nitrogen 0°C (1h) and 25°C (6h) using pyridine as acid scavenger. The reaction mixture was heated at 180°C (12h) using o-dichlorobenzene as the azeotroping agent to yield 5; mp 335°C. Sodium hydride and 5 were stirred in both NMP and 1-cyclohexyl-2-pyrrolidinone (CHP) under nitrogen at 25°C (4h). The reaction mixtures were heated at 180°C (24h) (NMP) and 250°C (CHP). A yellow precipitate was observed for both systems. The reaction mixtures were cooled, precipitated into excess methanol, the precipitates washed twice with methanol and dried in a vacuum oven for 24 hours to give 6 in good yields.

Results and Discussion

The imide ring remained intact throughout the synthesis of the phthalimide derivatives as indicated by absorbances in the IR at 1770-1790, 1715-1725 and 735-740 cm^{-1} . The nitrophenol structures were confirmed by IR absorbances around 1550 and 1340 cm^{-1} (NO_2), plus a broad stretch in the -OH region suggesting internal hydrogen bonding with the NO_2 group. Reduction of the NO_2 group was confirmed by the appearance of peaks at 3498 (NH_2), 3370 and 1387 (OH) cm^{-1} , for the model compounds, and a convoluted absorbance from 3550 to 3150 and 1398 cm^{-1} for the monomer precursor. The ^{13}C NMR chemical shift assignments for the model compounds are given in Table 1. These were used to confirm peak positions of the monomer precursors.

Monomer and polymer syntheses are illustrated in Scheme 1. Monomer structure was confirmed by IR peaks at 1771, 1718 and 740 cm^{-1} (imide), 1616 cm^{-1} ($C=N$: oxazole) and 1392 and 1243 cm^{-1} (-OH). The ratios of the IR peaks at 1392 cm^{-1} (OH in-plane bend) and 1243 cm^{-1} (C-O stretch) of the monomer were qualitatively compared to the intensities and areas of the repeat unit IR peaks at 1376 and 1248 cm^{-1} to evaluate polymer conversion and molecular weights (Figure 1).

Monomer structure was also confirmed by its ^{13}C NMR spectrum (H_2SO_4 , DMSO- d_6 insert) with peaks at 170.4 and 166.8 (F-C(Ar)), 167.5 and 166.9 (C=O: imide), 153.6 (HO-C(Ar)) and 151.0 ppm (oxazole ring carbon). A total of 20 peaks (3 split by fluorine) corresponding to 17 unique carbons were observed in the ^{13}C NMR spectrum (Figure 2). As with the IR, the intensities and areas of the ^{13}C NMR peak at 153.6 ppm (HO-C(Ar) end group, unique to the monomer) and the ^{13}C NMR peak at 154.1 ppm (internal Ar-O-Ar, unique to the repeat unit), were ratioed to estimate polymer conversion and DP. Under different reaction conditions, different DP products were obtained. Higher temperatures favor formation of higher chain extension before precipitation.

DSC analysis showed a thermal transition (endothermic) at 470°C (heating rate 10°C/min) versus 338°C for the monomer. Thermal decomposition is over 550° and the product polymers show promising physical properties. In addition, birefringence under the cross polarizing microscope confirmed crystallinity.

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Conclusions

We have obtained a series of phthalimide derivatives that were derived via nucleophilic aromatic displacement of chlorines at the 4 and 5-positions of the phthalimide substrate by the ambident nitrite ion. This procedure was quantitative as determined by ^{13}C NMR and TLC analysis. Solution reduction and simultaneous deprotection of the benzyloxy group using ammonium formate was also quantitative. The oxazole cyclization in NMP solution at 180°C gave the desired AB monomer. Polymerization of this monomer via nucleophilic displacement of the fluorine para to the benzoxazole 2-carbon by a phenolate anion has successfully given low molecular weight polymer due to insolubility. Higher polymerization temperatures possible with NMP (180°C) and CHP (250°C) increase the M_n ; use of NMP, CHP/LiCl, CaCl_2 solvent systems are being examined. The high enthalpies for imide and oxazole crystallization, combined with the planar structure of the imide-benzoxazole subunit apparently overwhelm the flexibility and catenation introduced by the oxygen in the polymer backbone, leading to polymer precipitation and low molecular weights. The thermal properties of these systems, however, are very promising. We are currently investigating stronger solvent systems and are synthesizing other derivatives that will give more backbone flexibility.

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CARBON	X = Cl; Y = Cl	X = OH; Y = NO ₂	X = OH; Y = NH ₂
1	+8.7	+28.4	+20.2
2	+8.7	+12.6	+15.8
3	-3.7	-7.7	-20.8
4	+2.8	-1.4	-4.0
5	+2.8	+7.5	-9.7
6	-3.7	-15.1	-21.9
7	(164.0)	(165.3)	(167.5)
8	(164.0)	(165.2)	(167.4)
A	+2.4	+3.2	+4.0
B	-2.3	-1.4	-1.6
C	-0.4	+0.3	+0.1
D	-1.0	-0.4	-1.3

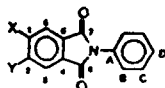
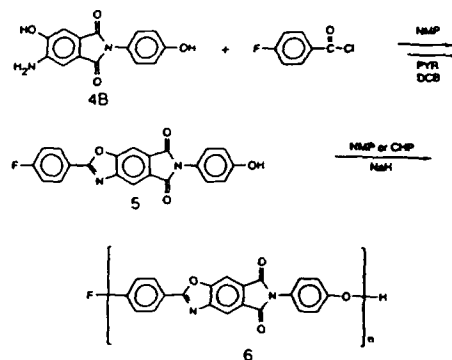


Table 1: ^{13}C NMR incremental chemical shift values of 4,5-disubstituted-N-phenylphthalimide (values are in ppm downfield from $\text{dms}\text{-d}_6 = 39.5$).



Scheme 1: Monomer and polymer syntheses.

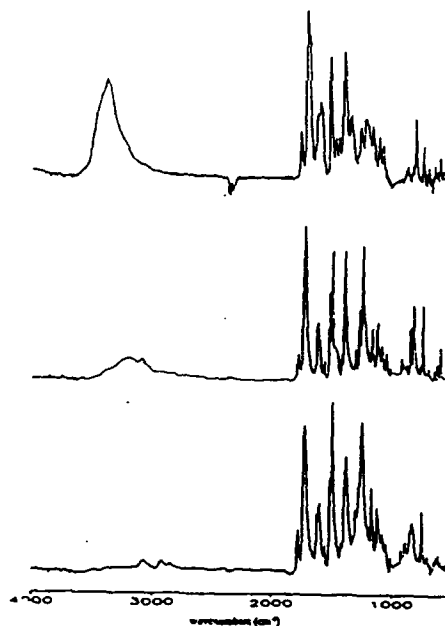


Figure 1: FT-IR spectra of monomer precursor 4B (top), monomer 5 (middle) and polymer 6 (bottom).

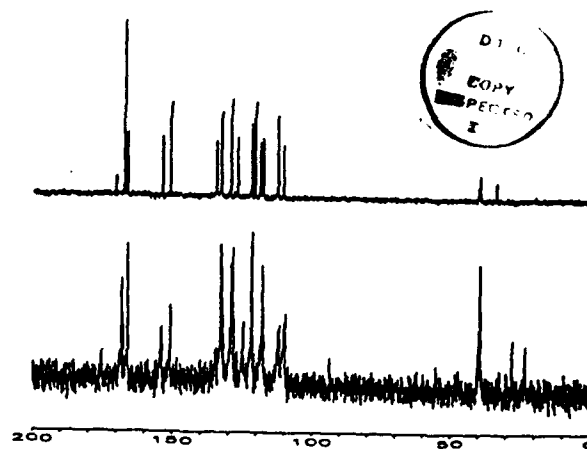


Figure 2: ^{13}C NMR spectra of monomer 5 (top) and polymer 6 (bottom).

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